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5 Pollux Drive
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MEMORANDUM FOR PRS (Contractor/In-House Publication)

FROM: PROI (TI) (STINFO) 24 Oct 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-205**
Suri, Suresh; Tinnierllo, M. & Marcischak, J. (ERC), "Synthesis and Screeniing of Advanced Hydrocarbon Fuels"

2000 USAF High Energy Density Matter (HEDM) Contractors Conference (Statement A)
(Park City, UT, 24-26 Oct 2000) (Deadline: PAST)

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Synthesis & Screening of Advanced Hydrocarbon Fuels

Suresh C. Suri*, Michael Tinnirello[1] & Jacob Marcischak[1]

**Air Force Research Laboratory/PRSP; [1]ERC Inc.*

10 East Saturn Blvd., Edwards Air Force Base, CA 93536

Presentation Outline

- **Goal**
  - HEDM program
  - NASA program
  - IHPRPT program (propellant perspective)
- **Criteria for fuel selection**
- **Approach**
- **Results**
- **Accomplishments** (FY-2000)
- **Planned Efforts** (FY-2001)

HEDM Goal

- **To Develop fuels with increased Isp over LOX/RP-1**
  - LOX/RP-1 (Calculated Isp) = 300 sec
  - LOX/RP-1 (Delivered Isp) = 263 sec

Determined at sea level and 1000 psi chamber pressure

IHPRPT GOAL
(PropellantContribution)

To Meet IHPRPT Phase II and Phase III Objective

Phase	Time	Improvement Over SOTA* Isp (del)
II	2005	+ 5 Sec
III	2010	+ 11 Sec

*SOTA: LOX/RP-1 Propellant Isp(del) = 263 Sec.
Isp (calc) = 300 Sec.

NASA Goal

- **FY-1999**
  - Deliver three advanced hydrocarbon fuel in 8-10 lb quantity.
    - Quadricyclane
    - 1,7-Octadiyne
    - Bicyclopropylidene
- **FY-2000**
  - Screen four hydrocarbons for their physical and hazardous properties.

Criteria for Fuel Selection

- **Predicts better performance (Isp) over LOX/RP-1 system**
- **Most desirable physical properties**
  - Lower vapor pressure compared to RP-1
  - Higher density (≥ RP-1 = 0.801 g/ml)
  - Freezing point (≤ -10 °C; RP-1 = -41.4 °c)
  - Boiling point ≥ B. P. Of RP-1
- **Storable**
- **Compatible with the current system**

Approach

- **Structural requirements**
- **Survey of energetic hydrocarbons**
- **Selection of hydrocarbons based on improved theoretical performance**
- **Synthesis of target hydrocarbons at bench scale.**
  - *Easy preparation, cost effective and safe*
- **Translate bench-scale synthesis to pilot scale.**

Heat of Formation of Saturated Hydrocarbons

Compound	Structure	ΔHf (Obs)
Ethane	CH_3CH_3	-20.04
Propane	$CH_3CH_2CH_3$	-25.02
Butane	$CH_3(CH_2)_2CH_3$	-30.03
Pentane	$CH_3(CH_2)_3CH_3$	-35.08

- ΔHf/added CH_2 = ~ -5 Kcal/mole

Heat of Formation of Unsaturated Hydrocarbons

- **Compound** **Structure** **ΔHf(Obs)**
- Ethylene $CH_2{=}CH_2$ +12.5
- 1,3-Butadiene $CH_2{=}CH{-}CH{=}CH_2$ +26.11
- $\Delta Hf/C = \sim +6.25$ Kcal/mole
- Acetylene $HC{\equiv}CH$ +54.36
- $\Delta Hf/C = \sim +27.1$ Kcal/mole

Structural Requirement for High Energy Contents (Cont..)

- The energy content is also increased by incorporating strain in the molecule
  - Ring compound — ΔHf
  - Cyclopropane — + 12.73 kcal/mole
  - Cyclobutane — + 6.78 kcal/mole
  - Cyclopentane — - 18.44 kcal/mole

Structural Requirements For High Energy Contents (Summary)

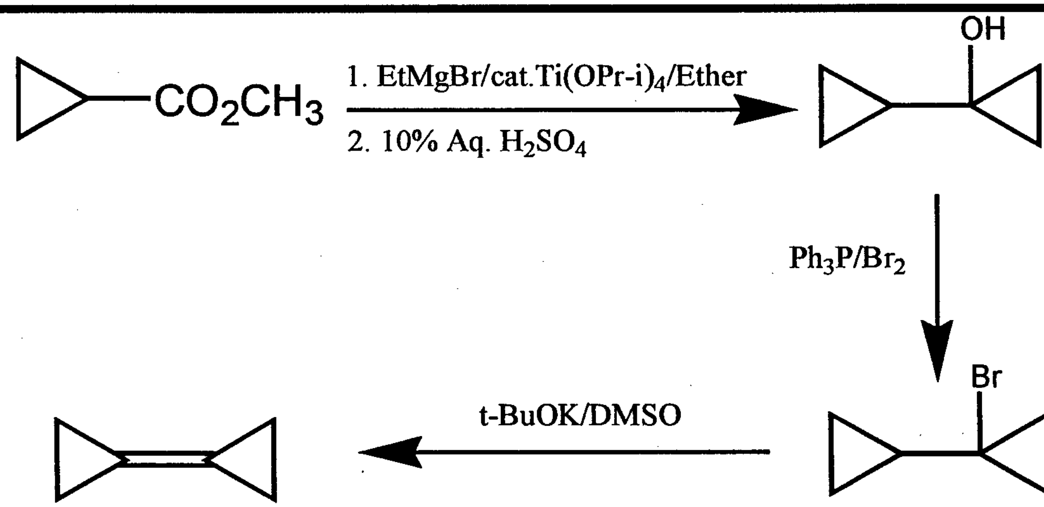
Incorporation of small ring (strain) and unsaturation in a molecule increases its energy contents

Performance Comparison of Energetic Hydrocarbons (Theoretical)

Hydrocarbons	H/C ratio	Density (g/ml)	Calc. ΔHf (Kcal/mole)	Calc. Isp (sec)
RP-1	1.9	0.80	-5.76	300.0
Quad	1.14	0.98	72.2	307.0
BCP	1.33	0.85	76.1	312.5
AFRL-1	1.2	0.77	64.0	311.3
AFRL-2	1.25	0.87	73.4	307.2
AFRL-3	1.0	0.93	123.6	307.2
AFRL-4	1.0	-	129.6	321.4
AFRL-5	1.33	0.80	56.3	308.7

Results

Synthetic Sequence of BCP



1. A.de Meijere, S. I. Kozhushkov, T. Spaeth and N. S. Zefirov; *J. Org. Chem.* **1993**, 58, 502
2. S.C. Suri; *Technical Report PL-TR-97-3057*, **1997**, p 26

Characterization of BCP

Physical properties

B.P. = 101 °C

M.P. = -12 °C

F.P. = -6.4 °C

Density = 0.8454 g/ml

ΔHf (exp.) = 67.4 kcal/mole

ΔHf (calc.) = 76.1 kcal/mole

Hazardous properties

Zero card gap (negative)

Drop test > 200 kg/cm

Friction test 133 newton

Toxicity

(Inhalation LC50)

1.95 mg/L

Adiabatic Compression(psi)

3000	Neg.

Is BCP Hypergolic?

- **Qualitative Test**
  - BCP is found to be hypergolic using nitrogen tetroxide(NTO). Spontaneous reaction with visible flame.
  - Hypergolic with inhibited red fuming nitric acid (IRFNA) as oxidizers. (Darren M. Thompson, U.S. Army missile command).
- **Ignition Delay**
  - The work is in progress under SBIR phase-1 with TDA Research, Inc.

Synthesis of AFRL-1

- Two steps synthesis
- Involves readily available materials
- Yield in both steps is > 90 %

Characterization of AFRL-1

Physical Properties

B.P. = 52- 55 °C

Density = 0.77 g/ml

ΔHf (Exp.)= 67.4 Kcal/mole

ΔHf (Calc.)= 64.0 Kcal/mole

Hazardous Properties

"0" card gap (Negative)

Liq. Impact test > 200 Kg-cm

Friction Test 78 Newtons

Adiabatic Compression (psi)

3000	Neg.

Synthesis of AFRL-3

- One step synthesis from AFRL-1.
- Requires oxidative coupling of AFRL-1.
- Yield is 92 %.

Characterization of AFRL-3

Physical Properties

B.P. = 102 °C

M.P. = -13 °C

Density = 0.93 g/ml

ΔH_f (Calc.)= 123.6 kcal/mole

ΔH_f (Exp.)= 117.0 kcal/mole

Hazardous Properties

- "0" card gap (negative)
- Liq Impact test <20 kg-cm
- Friction Test = 64.8 Newton

Adiabatic Compression(psi)

500	Neg.
2000	Neg.
3000	Neg.

Synthesis of AFRL-5

- Higher homologue of AFRL-1
- Two step synthesis
- Yield in both steps is greater than 90 %

Characterization of AFRL-5

Physical properties

B.P. = 78 °C

M.P. = -92.8 °C

Density = 0.7957 g/ml

ΔH_f (Exp.) = 50.39 kcal/mole

ΔH_f (Calc.) = 56.3 kcal/mole

Hazardous properties

"0"card gap (TBD)

Liq. Impact Test > 200 kg-cm

Friction Test = 43.12 newton

Adiabatic Compression (psi)

3000	Neg.

Accomplishments (FY 00)

- Delivered four hydrocarbons to NASA/Marshall.
  - Cyclopropyl acetylene (AFRL-1).
  - Bicyclopropylidene
  - Quadricyclane
  - 1,7-Octadiyne
- Synthesized two advanced hydrocarbons(AFRL-1 & AFRL-3) at bench-scale level.
- 200 gm of AFRL-3 was synthesized in the laboratory.

Planned Efforts of Fiscal Year 2001 (Technical)

- To continue exploring <u>bench scale</u> synthesis of advanced hydrocarbon (AFRL-4).
- Evaluate physical & hazardous properties of AFRL-4 & AFRL-2.

Alliances

- **Industry**
  - Boeing
  - TRW
  - Kistler
  - Aerojet
- **NASA**
  - Marshall
  - Glenn
- **DOD**
  - Navy- China Lake
  - Army- Huntsville

Team Efforts

Research

- Suresh C. Suri
  Michael Tinnirello
  Jacob Marcischak

Theoretical Efforts

- Jeffrey Mills

Physical Properties

- Paul Jones, JoAnne Larue, Jeff Yinn

Hazardous Properties

- Tommy W. Hawkins, Adam Brand, Milton Mckay, Ismail Ismail

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